OPTICAL MODULATION SPECTROSCOPY OF a-Si:H BASED MULTILAYER STRUCTURES

T.X. ZHOU*, H. STODDART*, Z. VARDENY*, J. TAUC* AND B. ABELES**
* Department of Physics and Division of Engineering, Brown University, Providence, RI 02912
** Exxon Research and Engineering Company, Annandale, NJ 08801

ABSTRACT

Steady state optical modulation spectrum of a–Si:H/a–SiN_x:H multilayer structure, its temperature dependence and time decay have been studied. For multilayers with very thin sublayers the onset of the spectrum is more gradual and occurs at higher energy than the spectrum for unlayered a-Si:H, indicating a broadening of the band tail. For larger layer thicknesses the optical modulation spectrum is compared to that for P-doped a-Si:H and interpreted as due to charged dangling bonds at the interfaces.

INTRODUCTION

The optical modulation spectroscopy (OM) is a powerful optical means to study states in the mobility gap, relaxation and recombination processes of photogenerated carriers in amorphous materials.[1] We have applied the steady state OM technique to a–Si:H/a–SiN_x:H multilayer structures (MLS) which are known to have quite uniform layers and relatively abrupt interfaces.[2,3] We find that the photocarrier properties in MLS with Si sublayer thickness d_S<20 Å are dominated by strong disorder which results in substantial band tail broadening. This produces a shift of the band tail related induced absorption towards higher energies and a weaker temperature and time dependence compared to unlayered a-Si:H. For the MLS with d_S>20 Å we find a slower and less temperature dependent recombination than in unlayered a-Si:H. The OM spectrum and its time decay are very similar to those in singly doped a-Si:H where they have been associated with carriers trapped at charged dangling bonds and impurities. From this comparison we identify the interface-related deep defects as charged dangling bonds.

EXPERIMENTAL

Two light sources are needed for the OM spectroscopy[1]: a pump beam for photogeneration of carriers and a probe beam for measuring the photo-induced changes in transmission. The pump was a chopped (f = 75 Hz) Ar^+ laser beam with an adjustable intensity from 1 to 100 mW/cm^2, while the probe beam was an incandescent light source dispersed by a monochromator. The transmission T and its modulation ΔT were recorded simultaneously using InSb, Ge and Si detectors and lock-in amplifiers. The pump for the transient measurements was a dye laser producing pulses of 10 nsec duration with a power of 400 μJ at 2.1 eV and a repetition rate of 20 Hz. $\Delta T(t)$ from 100 nsec to 50 msec was measured in the energy range of 0.8 to 1.1 eV using a Ge detector, a silicon filter and fast electronics.

The a–Si:H/a–SiN_x MLS were prepared[2,4] using the plasma assisted chemical vapor deposition technique on polished c-Si or quartz substrate held at 240^{0}C. Pure SiH_4 was used for the a-Si:H sublayers and a 5:1 mixture of NH_3 and SiH_4 for the a–SiN_x:H sublayers. The repeat distance d for the MLS was varied while the ratio of the sublayer thicknesses d_S/d_N was kept constant at 0.85. The number of sublayers was adjusted so as to keep the film thickness approximately at 1 μm.

Mat. Res. Soc. Symp. Proc. Vol. 77. 1987 Materials Research Society

MULTILAYER STRUCTURES WITH $d_S < 20$ Å

Steady state OM spectra for the MLS with $d_S = 7$ Å and 10 Å measured at 80 K are shown in Fig. 1; a typical OM spectrum for an unlayered a-Si:H is also shown for comparison. The interference fringes which usually dominate the spectrum[5] (especially for the films deposited on quartz substrate) have been averaged out. It is apparent that the photoinduced absorption (PA) band gradually shifts to higher energy for smaller d_S, which is in agreement with the upward shift in the photoluminescence (PL) band[6] and in the energy gap.[1,6] It is also apparent in Fig. 1 that the onset of PA in the MLS with small d_S is more gradual and occurs at higher energy than the PA in the unlayered a-Si:H, indicating a broadening of the band tail. The reason for this is that photocarriers in a-Si:H with broader band tails are trapped in deeper states[7] and their energy distribution is wider as shown by the studies of PL in a–Si:H.[8] The band tail broadening for MLS with small d_S has been observed also in other measurements such as optical absorption[4] (the Urbach tail broadens) and PL[6] (band width broadens). This has been attributed to an increase in disorder as verified by Raman scattering[9] that exhibits increase in the phonon line widths.

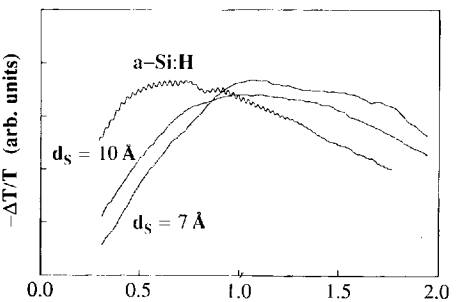

Fig. 1 OM spectra for MLS with $d_S = 7$ Å and 10 Å measured at 80 K compared with OM for unlayered a-Si:H at 10 K.

The increased disorder and the broadened band tail for small d_S strongly influence the recombination kinetics of the photocarriers. The PA strength at 0.33 eV for $d_S = 7$ Å and 10 Å as a function of temperature is shown in Fig. 2 and is compared to that for an unlayered a-Si:H. Since the PA strength is proportional to the steady state density of photogenerated carriers which depends on the recombination rate,[1] the relatively weak temperature dependence for MLS indicates that the photocarrier recombination is not governed by a thermally activated process as in unlayered a–Si:H.[1] A plausible explanation for this is that the photocarriers thermalize among the band tail states by directly hopping down to lower energies[7] rather than by thermal release into delocalized states at higher energies and consequently retrapped at deeper levels. We also observed that the decay of PA in the MLS with small d_S is less temperature dependent than in unlayered a-Si:H, indicating that the recombination is probably dominated by hopping even at elevated temperatures.

MULTILAYER STRUCTURES WITH $d_S > 20$ Å

As shown in Fig. 3, the OM spectrum for the MLS with larger layer thickness is significantly different from that of the thinner layer samples (Fig. 1): the onset and the maximum of the PA band is shifted to lower energies. A second PA onset is seen near 1.2 eV

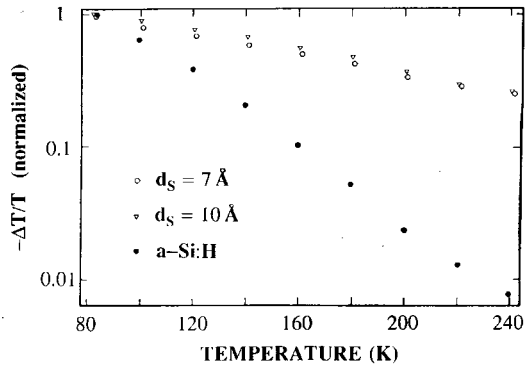

Fig. 2 Temperature dependence of the PA strength for MLS with d_S = 7 Å, 10 Å and for an unlayered a-Si:H.

which does not appear in the OM spectrum of the unlayered a-Si:H. We note that when d_S increases from 25 Å to 204 Å the OM spectrum remains almost unchanged instead of approaching that of the unlayered a-Si:H. This strongly indicates that the layer interfaces dominate the OM spectra in the MLS. This is in agreement with the observation[4] that strong internal electric fields are present in the sublayers which tend to separate photocarriers.[10] In fact the picosecond PA measurements[11] in the MLS with d_S varying from 25 Å to 204 Å indeed show that photocarriers arrive at the interfaces in less than 100 psec at 300 K (10 ns at 80 K). We therefore believe that the spectra for the MLS with $d_S > 20$ Å are determined by the interface related states in the gap.

Also shown in Fig. 3 is the OM spectrum of an unlayered P-doped a-Si:H (prepared with 10^{-3} PH_3/SH_4 gas ratio) and the resemblance between the two OM spectra is apparent. The OM spectrum of the P-doped a-Si:H has been associated[12,13] with charged impurities (P_4^+) near the conduction band with a PA band at 0.3 eV and charged dangling bond states (D^-)

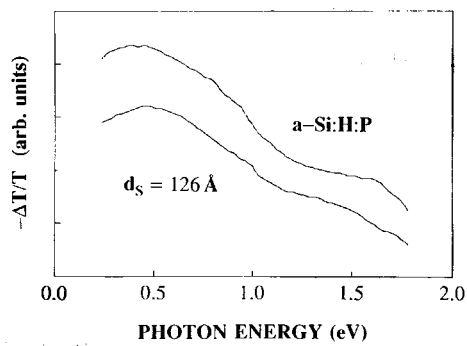

Fig. 3 OM spectrum for MLS with d_S = 126 Å compared with that of P-doped a-Si:H at 80 K.

which introduce a second PA band around 1.2 eV. Figures 4 and 5 show that the temperature dependence and time decay of PA in MLS with d_S = 25 Å and in the P-doped a-Si:H are also very similar. In addition, the decays are slow and depend very little on temperature in both materials.

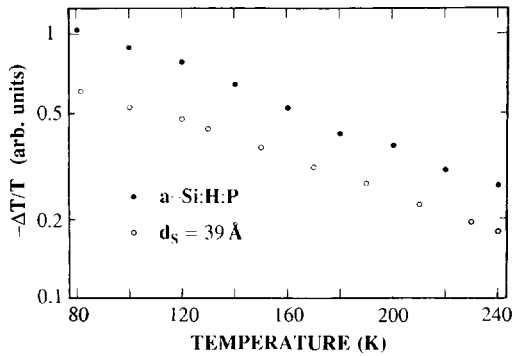

Fig. 4 Temperature dependence of PA at 0.33 eV in MLS with d_S = 39 Å and in P-doped a-Si:H.

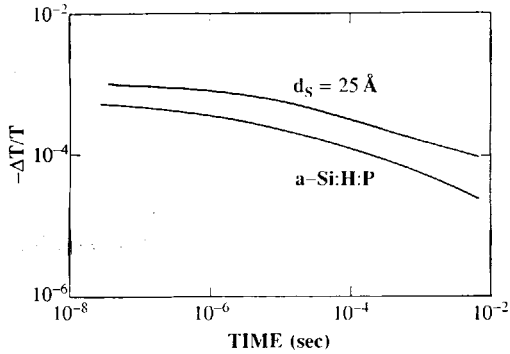

Fig. 5 Time decay of PA in MLS with d_S = 25 Å and in P-doped a-Si:H at 80 K.

Since the photocarriers arrive at the interfaces shortly after excitation,[11] the steady state OM measurements are more sensitive to the interface-related defects than to the bulk defects. We propose that the first PA band near 0.3 eV is due to electrons trapped above the Fermi level and that the second PA band around 1.2 eV is due to holes trapped at the negatively charged defects at the interfaces. An alternative interpretation for the first PA band is that it results from photo-excited electrons trapped at positively charged interfacial states associated with the nitride. These states may be close in energy to the intrinsic defect levels in the a–SiN_x:H sublayer[14] (2.4 eV above the nitride valence band) which are located near the conduction band edge in the silicon sublayers. In either case, we identify the negatively charged

states near the interfaces as doubly occupied dangling bonds. This suggestion is based on the similarities of the PA properties between P-doped a-Si:H and MLS which include similar spectral features, temperature dependence and decay curves. We interpret the slow PA decay in MLS as a consequence of charge separation by the internal fields,[10] which is consistent with the suggestion by Street et al.[15] that the slow recombination in singly doped a-Si:H may be due to charge separation.

ACKNOWLEDGEMENT

The authors thank T. R. Kirst and L. Chen for technical assistance. The work was supported in part by NSF grant DMR 82-09148 and benefited from the use of the Optical Facility of NSF Material Research Laboratory at Brown University.

REFERENCES

[1] J. Tauc, Festkoerperprobleme Vol. XXII, p. 85 (Vieweg, Braunschweig, 1982).

[2] B. Abeles and T. Tiedje, Phys. Rev. Lett. 51, 2003 (1983).

[3] N. Ibaraki and H. Fritzsche, Phys. Rev. B 30, 5791 (1984).

[4] C. B. Roxlo and B. Abeles, Phys. Rev. B 34, 2522 (1986).

[5] P. O'Connor and J. Tauc, Phys. Rev. B 25, 2748 (1982).

[6] T. Tiedje, B. Abeles and B. G. Brooks, AIP Conf. Proc. #120 (edited by P. C. Taylor and S. G. Bishop), p. 417 (1984).

[7] D. Monroe, Phys. Rev. Lett. 54, 146 (1985).

[8] D. J. Dunstan and F. Boulitrop, Phys. Rev. B 30, 5945 (1984).

[9] N. Maley and J. S. Lanin, Phys. Rev. B 31, 5577 (1985).

[10] K. J. Chen and H. Fritzsche, Bull. Am. Phys. Soc. 31, 333 (1985).

[11] H. T. Grahn, H. A. Stoddart, T. Zhou, Z. Vardeny, J. Tauc and B. Abeles, Proc. 18th Int. Conf. on the Physics of Semiconductors, Stockholm, 1986 (in press).

[12] I. Hirabayashi, K. Morigaki, S. Yamasaku and K. Tanaka in Ref. 6, p. 8.

[13] T. X. Zhou, Z. Vardeny and J. Tauc, to be published.

[14] C. B. Roxlo, T. Tiedje and B. Abeles, in Ref. 6, p. 433.

[15] R. A. Street, D. K. Biegelsen and R. L. Weisfield, Phys. Rev. B 30, 5861 (1984).